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In situ control of As dimer orientation on Ge(100) surfaces

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We investigated the preparation of single domain Ge(100):As surfaces in a metal-organic vapor phase epitaxy reactor. *In situ* reflection anisotropy spectra (RAS) of vicinal substrates change when arsenic is supplied either by tertiarybutylarsine or by background As_4 during annealing. Low energy electron diffraction shows mutually perpendicular orientations of dimers, scanning tunneling microscopy reveals distinct differences in the step structure, and x-ray photoelectron spectroscopy confirms differences in the As coverage of the Ge(100):As samples. Their RAS signals consist of contributions related to As dimer orientation and to step structure, enabling precise *in situ* control over preparation of single domain Ge(100):As surfaces. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4754122]

Vicinal Ge(100) is the standard substrate for high-performance triple junction solar cells usually grown in metal-organic vapor phase epitaxy (MOVPE) environment.[1] Ge(100) surface preparation prior to III-V nucleation plays an important role for the subsequent quality of III-V layers due to defect formation at the crucial Ge(100)/III-V heterointerface.[2] Growth of polar III-V material on non-polar Ge substrates requires single domain surfaces where only a single dimer orientation occurs to avoid anti-phase domains (APD).[3] Depending on step height, dimer orientation is either preserved from terrace to terrace for even numbered atomic step heights or alternates for odd numbered atomic step heights. Vicinal Ge(100) substrates with 6° offcut tend to form a single-domain surface with double layer steps after deoxidation in H_2 ambient of a MOVPE reactor.[4] The surface structure of vicinal Ge(100) strongly changes by exposure to As[5–7] which is important for GaAs nucleation.[8–11]

Main characteristics of Ge(100):As surfaces are the preferential As dimer orientation, the height of steps, and the atomic configuration at the step edges.[5,6] In analogy to Si(100),[12] As atoms adsorb on the Ge(100) surface and form As dimers, oriented either parallel or perpendicular to the step edges. Here, we denote terraces of type A with (1×2) reconstruction as $\mathrm{Ge(100):As}_{\perp}$ due to As dimers being aligned perpendicular to the step edges, and terraces of type B with (2×1) reconstruction as $\mathrm{Ge(100):As}_{\parallel}$ for As dimers parallel to the step edges. Process temperature, source, and partial pressure of arsenic are important parameters for the Ge(100):As surface preparation.[5,6] In MOVPE ambient, As can be supplied either directly via precursors such as AsH_3 and TBAs, or indirectly as background As_4 originating from the reactor environment covered by As precursor fragments. AsH_3 annealing may induce significant step bunching and ridge formation due to etching of the Ge surface dependent on temperature and partial pressure.[5,6] Ge(100):As surfaces prepared in either AsH_3 or background As_4 show a (2×1) and (1×2) majority domain, respectively, and deviate in step structure.[5,6] GaAs growth studies on Ge(100) by Refs. 8 and 10 indirectly showed the crucial influence of the surface preparation by As exposure on the quality of the subsequent GaAs nucleation layer. Ref. 12 highlights the impact of the preparation route on the resulting domain and step structure on vicinal Si(100):As by scanning tunneling microscopy (STM) measurements.

We employ *in situ* reflection anisotropy spectroscopy (RAS) for direct characterization of Ge(100):As surfaces during MOVPE processing. Similar to RAS of Si(100),[13,14] the vicinal Ge(100) surface exhibits characteristic RAS signals for both the clean[15,16] and the monohydride terminated surface.[4] Ref. 17 demonstrates the sensitivity of RAS to the As dimer orientation on the surface of As terminated Si(100) with 4° offcut. Defined by

$$\frac{\Delta r}{r} = 2\,\frac{r_{[0\bar{1}1]} - r_{[011]}}{r_{[0\bar{1}1]} + r_{[011]}}, \tag{1}$$

the RAS signals associated with mutually perpendicular dimer orientations exhibit opposite signs. Since RAS integrates over the entire probed surface area, the measured signal reflects the preferential dimer orientation quantitatively.[18]

In this letter, we present *in situ* RA spectra of $\mathrm{Ge(100):As}_{\parallel}$ and $\mathrm{Ge(100):As}_{\perp}$ surfaces prepared by exposure to TBAs and background As_4, respectively. We measured low energy electron diffraction (LEED), STM, and x-ray photoelectron spectroscopy (XPS) on our Ge(100):As samples to correlate the surface properties with the observed RA spectra. While LEED confirmed mutually perpendicular preferential dimer orientations, STM revealed distinct differences in the step structure, and XPS showed the purity and varying As coverage whether samples were exposed to TBAs or background As_4. The RA

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spectra of vicinal Ge(100):As surfaces contain contributions related to both the As dimers and to the step structure. In particular, the sensitivity to As dimer orientation enables precise *in situ* control over preparation of single domain Ge(100):As surfaces.

Sample preparation took place in an Aixtron AIX-200 MOVPE reactor equipped with an *in situ* RA spectrometer (LayTec EpiRAS 200). We cleaned reactor parts (liner, susceptor) and sample carriers with regard to III-V residuals to avoid unintentional contamination of the samples. A dedicated MOVPE-to-UHV sample transfer system enabled contamination-free access to surface science tools[19] such as LEED (Specs ErLEED 100-A), STM (Specs Aarhus 150), and XPS (Specs Focus 500 and Phoibos 100). We used Ge(100) substrates with 6° misorientation towards [011] direction specified as "epiready" (supplier: AXT) and prepared the samples without any wet-chemical pre-cleaning. The MOVPE preparation was carried out under H_2 process gas and a reactor pressure of 100 mbar for all samples shown here. Annealing at 700 °C for 20 min removed oxides and other contamination from the "epiready" substrates.[4] According to Ref. 5, annealing in AsH_3 at temperatures around 650 °C leads to the formation of a $Ge(100):As_{\perp}$ surface whereas annealing in background As_4 results in $Ge(100):As_{\parallel}$. In contrast, we used TBAs as As precursor (partial pressure 2.72×10^{-2} mbar). Background As_4 was indirectly supplied by the inner MOVPE reactor walls when stopping the TBAs flow.

Figure 1 shows RA spectra of the $Ge(100):As_{\parallel}$ (red line) and the $Ge(100):As_{\perp}$ surface (green line) measured at 50 °C (dimer orientation confirmed by LEED and STM, see below). Preparation of the $Ge(100):As_{\parallel}$ surface consisted of exposure to TBAs for 10 min at 670 °C, cooling to 300 °C under TBAs supply and additional annealing at 500 °C for 5 min without TBAs supply before cooling to 50 °C. In contrast, the $Ge(100):As_{\perp}$ sample was annealed for 15 more minutes at 670 °C without TBAs supply (after initial TBAs exposure), before cooling to 50 °C.

Both *in situ* RA spectra exhibit similar line shape but opposite sign. In particular, between 1.5 and 3.1 eV, we observed a sharp local extremum around the critical point energies E_1 and $E_1 + \Delta_1$ at 2.1 eV (blue arrow) and a broad shoulder at around 2.6 eV. As shown for Si(100):As,[17] mutually perpendicularly oriented dimers induce an inversion of the RAS signal when step contributions are negligible. The coexistence of dimers with mutually perpendicular orientation reduces the amplitude of RAS peaks and enables domain quantification by linear scaling.[18] Scaling of the $Ge(100):As_{\parallel}$ spectrum to the $As_{\perp}$ spectrum by a factor of −1.38 (dotted red line) matches the intensities of the peak around 2.1 eV, but also reveals explicit differences between both spectra (small gray arrows): the maximum of the $Ge(100):As_{\perp}$ spectrum at 2.1 eV is slightly shifted (0.05 eV) towards higher energies compared to the $Ge(100):As_{\parallel}$ spectrum; above 3.1 eV, the $Ge(100):As_{\parallel}$ surface exhibits a minor peak around 3.5 eV, whereas the $Ge(100):As_{\perp}$ surface features a small shoulder at 3.2 eV and a stronger peak around 3.9 eV with higher intensity.

Beyond the type of surface reconstruction, the step structure may also contribute to the RA spectra.[20,21] On vicinal (100) surfaces, step-related RAS contributions depend on the step density,[21] and the atomic configuration of the steps.[20] According to Ref. 5 and 6, preparation parameters strongly influence the step structure of As exposed Ge(100):As surfaces. We assign the peak structure around 2.1 eV in the RA spectra of both Ge(100):As surfaces to the As dimers and its sign to their orientation (blue arrow), while the significant qualitative differences between the spectra (gray arrows) might be related to different step structures. We measured LEED, STM, and XPS on our Ge(100):As samples to correlate the surface properties with the observed RA spectra.

Figure 2 depicts LEED and STM results of the $Ge(100):As_{\parallel}$ sample. The LEED pattern (Fig. 2(a)) shows half-order spots with significantly stronger intensity in $[0\bar{1}1]$ direction as in [011] direction (see circles) indicating a preference for the (2×1) surface reconstruction domain—equivalent to the majority of As dimers oriented parallel to the step edges (see upper sketch in Fig. 1). Stripes along [011] direction indicate terraces of irregular width. The STM image of the $Ge(100):As_{\parallel}$ surface (Fig. 2(b)) shows dimer rows oriented perpendicular to the step edges, equivalent to parallel alignment of the As dimers. Steps run straight along $[0\bar{1}1]$ direction with a non-uniform step height distribution. Step bunching creates relatively large terraces (see line profile A to B in Fig. 2(c)) probably driven by etching processes during TBAs annealing.[6] Similar to samples prepared by AsH_3 annealing,[6] we observe a small ledge at the end of the dimer rows close to the edge (see arrow in Fig. 2(b)).

In contrast to the $Ge(100):As_{\parallel}$ sample, we recognize a clear preference for the (1×2) reconstruction in the LEED pattern of the $Ge(100):As_{\perp}$ sample (Fig. 3(a)). Half-order spots in [011] direction (see circles) correspond to a surface with As dimers on the terraces oriented perpendicular to the step edges (see lower inset of Fig. 1). Accordingly, we observed a prevalence for terraces with dimer rows oriented

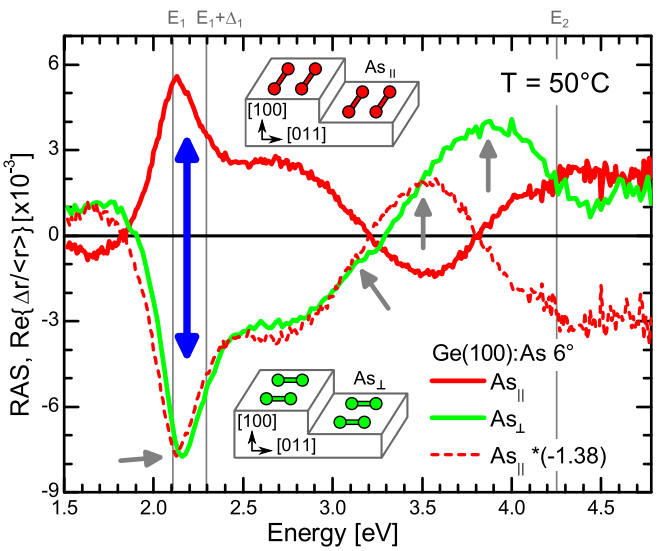

FIG. 1. *In situ* RAS of Ge(100):As 6° with predominant (2×1) (red) and (1×2) (green) surface reconstruction domains where dimers are oriented parallel ($Ge(100):As_{\parallel}$) or perpendicular ($Ge(100):As_{\perp}$) to the step edges, respectively. For comparison, the flipped and scaled (factor 1.38) RA spectrum of Ge(100):As 6° with predominant (2×1) reconstruction is also depicted. The insets illustrate the major As dimer orientation on the surface with respect to the step edges.

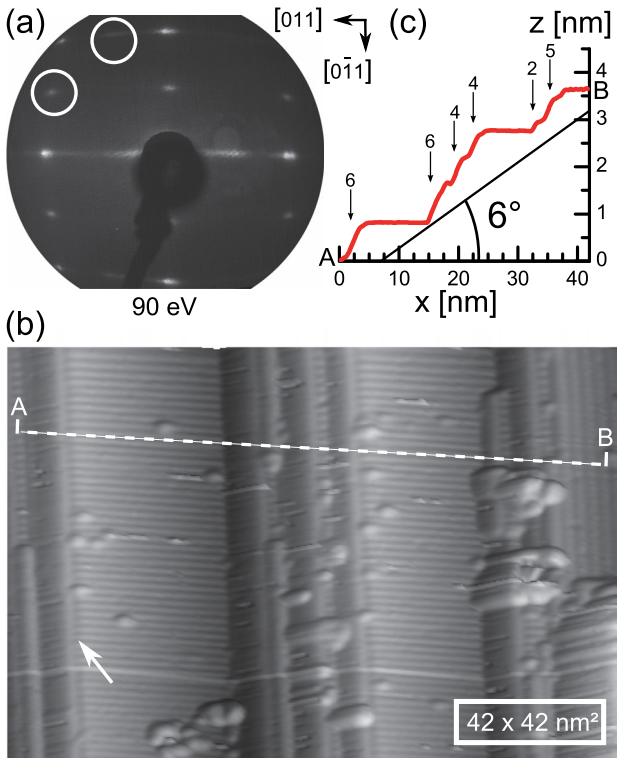

FIG. 2. LEED pattern (a) and STM image ($V_{sample} = -3.0\,V$, $I_t = 140\,pA$, artificially illuminated) (b) of the Ge(100):$As_{\parallel}$ surface shown in Fig. 1. (c) Presents a profile of the STM image from point A to B.

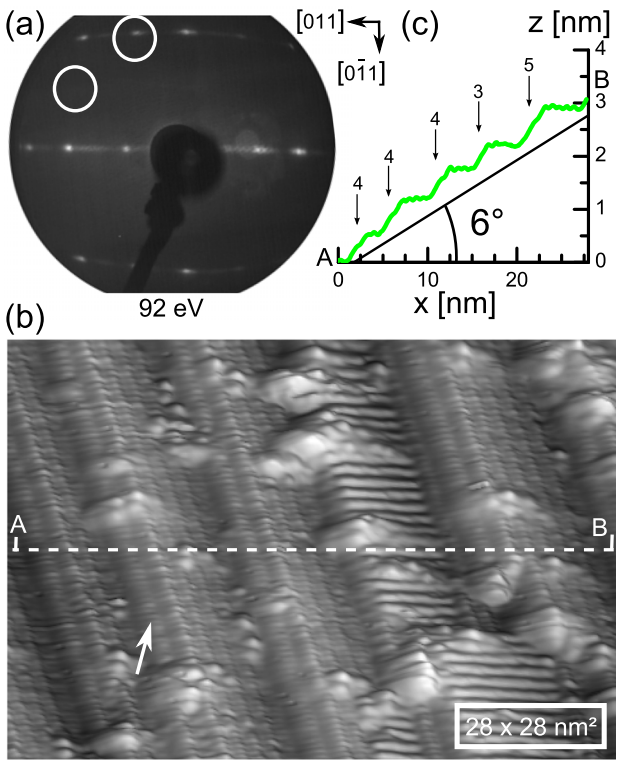

FIG. 3. LEED pattern (a) and STM image ($V_{sample} = -0.76\,V$, $I_t = 350\,pA$, artificially illuminated) (b) of the Ge(100):$A_{\perp}$ surface shown in Fig. 1. (c) Presents a profile of the STM image from point A to B.

along the step edge on the corresponding STM images (Fig. 3(b)). Note that Fig. 3(b) also exhibits few terraces with dimer rows perpendicular to the step edges. The line profile (Fig. 3(c) shows a more regular sequence of terraces and steps than Fig. 2(c). Similar to previous background As_4 studies[5] steps run straight along [0$\bar{1}$1], being mostly four layers high, and of A-type (4A steps). More precise comparison to the step reconstruction proposed by Refs. 5 and 6 is difficult due to limited STM resolution. On our samples (see arrow in Fig. 3(b)), the edge of the upper terrace of the 4A steps coincides with the maximum of the outermost dimer row of the terrace. The steps exhibit a small ledge near the centre of the slope to the lower terrace.

Both LEED patterns confirm the preparation of nearly single domain Ge(100):As surfaces, but with mutually perpendicular As dimer orientation. Amplitude and sign of the peak structure in the RA spectra between 1.5 and 3.2 eV correspond to the surface reconstruction and reflect the major As dimer orientation in agreement with the LEED results. The LEED patterns suggest the presence of a larger residual minority domain for the Ge(100):$As_{\perp}$ sample, in good agreement with observation of higher RAS intensity around 2.1 eV in the RA spectra (Fig. 1) compared to the data of the Ge(100):$As_{\parallel}$ surface. The characteristics of the line shape in the RA spectra (grey arrows in Fig. 1) may arise from structural differences on the Ge(100):As surfaces (compare profiles and step edges indicated by arrows in Figs. 2 and 3 as shown for Si(100).[20,21] The occurrence of minority domain terraces on the Ge(100):$As_{\perp}$ sample is consistent with mutually perpendicular As dimers but also with selective As desorption revealing the underlying Ge dimers.

We estimated and compared the As concentration on the Ge(100):$As_{\parallel}$ and Ge(100):$As_{\perp}$ samples by XPS employing the surface sensitive Ge $2p_{3/2}$ and As $2p_{3/2}$ photoemission lines. Normalization by matching the intensities of the Ge 3d line, which is a less surface sensitive peak, facilitates a direct comparison of the data (Fig. 4). The Ge $2p_{3/2}$ and As $2p_{3/2}$ line shapes of both samples are equal without an indication for As-Ge bonds in terms of a chemical shift (most probably below our experimental resolution). However, the Ge(100):$As_{\parallel}$ surface shows a significantly higher intensity in the As $2p_{3/2}$ photoemission line (Fig. 4(b)). Based on the intensity ratio of the core level intensities (As $2p_{3/2}$ to Ge $2p_{3/2}$) and assuming a simple two-layer model and an electron mean free path of 9 Å for the utilized energy range,[22,23] we estimated the As coverages for the different samples: We obtained about 1.0 monolayer (ML) and about 0.7 ML As for the Ge(100):$As_{\parallel}$ and Ge(100):$As_{\perp}$ surface, respectively. Given the surface sensitivity of the XPS, arsenic diffusion into the Ge substrates[24] cannot fully explain the significant differences of the estimation. Arsenic is known to cover Ge(100) by a monolayer forming a chemically passivating surface reconstruction,[6] and might desorb from the Ge surface during annealing at 670 °C in background As_4.[7] However, also excess As adsorption might occur during TBAs in direct analogy to excess phosphorus accumulation on GaP(100) surfaces.[25] Considering the high step density on vicinal substrates, the As coverage of the steps edges might have an impact, too. Our STM images show multiple layer steps due to step bunching for Ge(100):$As_{\parallel}$, whereas 4A steps prevail on Ge(100):$As_{\perp}$. Since we also identified very

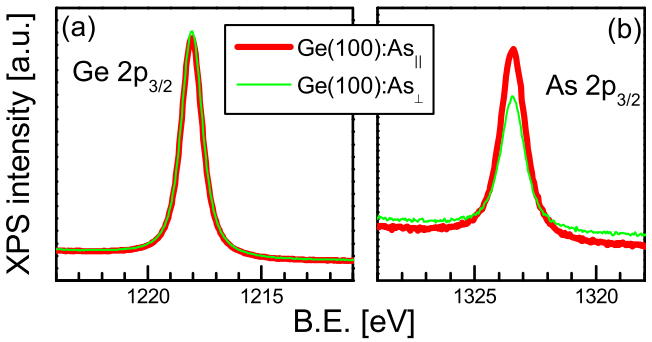

FIG. 4. XP spectra of Ge(100) : $As_{\parallel}$ and Ge(100) : $As_{\perp}$ in the range of the Ge $2p_{3/2}$ and As $2p_{3/2}$.

different step types (compare step edges at arrows in Figs. 2(b) and 3(b)) on both surfaces, differences in the As coverages appear at least conceivable.

We established the characteristic RA spectra of vicinal Ge(100):As surfaces. Correlation of the RA spectra with results from LEED, STM, and XPS revealed the atomic structure of the MOVPE prepared Ge(100):$As_{\parallel}$ and Ge(100):$As_{\perp}$ surfaces. Both dimer orientation and step structure influence the RA spectra. Hence, RAS enables *in situ* monitoring of the As dimer orientation during MOVPE processing. Currently, we concentrate on precise determination of process parameters for full control of dimer orientation and surface structure. In particular, we intend to correlate surface preparation with quality of III-V nucleation and ultimately with device performance.

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